Dissolved nickel and benthic flux in South San Francisco Bay: A potential for natural sources to dominate

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Aqueous concentrations of nickel in the southern component of San Francisco Bay (South Bay) have periodically exceeded the water-quality criteria (8.2 ppb Ni) established in accordance with the EPA's Clean Water Act. Nickel-rich serpentinite formations around the San Francisco Bay-estuary, particularly South Bay, are eroded, transported and accumulated in estuarine sediments, providing a natural source of nickel (Fig. 1). Although the areal coverage of these formations is not pronounced, their potential importance is suggested by the spatial distribution of serpentinite throughout nearly all watersheds surrounding South Bay. This non-anthropogenic source, as well as the intermittent exceedances in South Bay nickel concentrations, has motivated a reexamination of potential nickel-transport processes and regulatory strategies.

MATERIALS AND METHODS

Field and laboratory studies between April 1998 and May 1999 were conducted to provide the first direct measurements of the benthic flux of dissolved nickel in South Bay (Topping et al. 2001). Two to four sediment cores at each station were acquired during each field trip, and were subsequently transported to the laboratory for incubation in darkness (to mitigate photosynthetic activity). Time-incremented samples of the overlying water in each core were analyzed for various chemical, physical and biological parameters that potentially affect nickel remobilization. The benthic-flux estimates for nickel were calculated directly from the change in dissolved-nickel concentrations over the 12-hour incubation. Supporting studies were performed from October 1999 through April 2002 using identical methods. Although there is no comparative metal-flux data to corroborate our methods, Caffrey et al. (1996) found that *in-situ* flux chamber measurements agreed with those from core incubations for nutrient flux in South Bay.

All analytical data for trace metals were provided by on-line iminodiacetate resin concentration prior to analysis by ICP-MS (Topping and Kuwabara 1999). This method eliminates salt-water matrix effects in a three-step process: adsorption of the metals to the chelating resin, elution with nitric acid, and transportation of the

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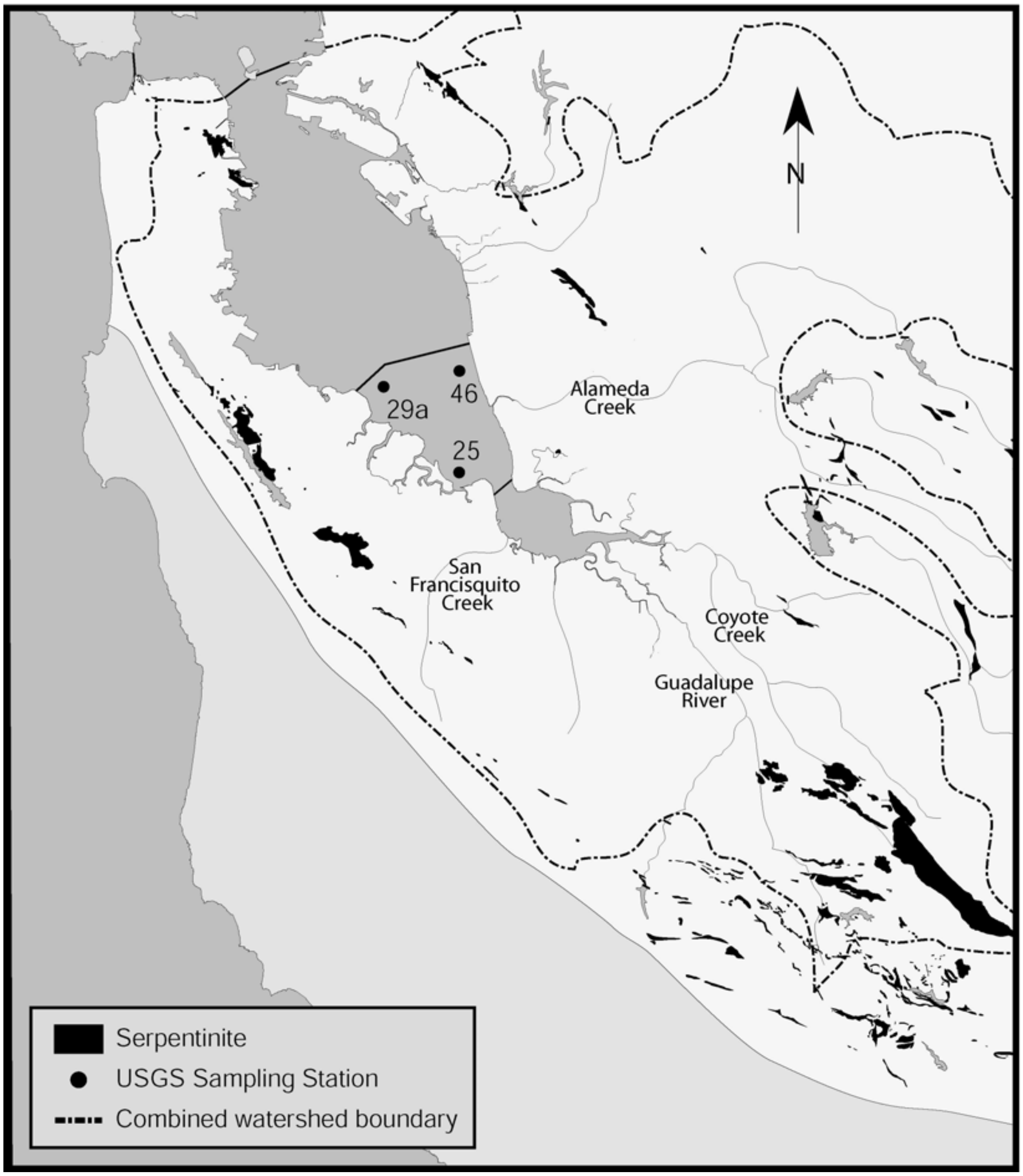

Figure 1. Serpentinite formations in the watersheds surrounding South San Francisco Bay. (Modified from Robert Coleman, Stanford University)

eluent directly to the instrument. The robustness of the method is assured by sample replication, and by the authors' participation in an inter-laboratory study (Willie 2000). Method detection limits for nickel were ~0.15 ppb, and nickel recoveries for the certified reference material SLEW-2 were between 90-100% for the data discussed below.

RESULTS AND DISCUSSION

In 1998, San Francisco Bay was listed in non-compliance with the Clean Water Act of 1972 because concentrations of particle-associated (total recoverable) nickel and copper occasionally exceeded regional and national criteria. Concern about the impairment of aquatic resources in the estuary due to elevated nickel and copper concentrations motivated a number of toxicological and geochemical studies to examine whether site-specific adjustments to the criteria were warranted. Criteria based on these studies are intended to facilitate the development of load-allocation strategies (TMDL plans) assuming that the factors controlling the fate of input contaminants like nickel are understood.

Unlike copper, which is locally input primarily from anthropogenic sources such as automotive brake debris and municipal plumbing, nickel has no anthropogenic source outside of treated industrial effluent. This contrast between solutes is evident when sediment trace-metal concentrations are compared between the highly urbanized South Bay and the minimally urbanized Tomales Bay just 40 miles northwest. Sediment concentrations for copper in South Bay are about twice that of Tomales, but the nickel concentrations are similar (Tetra Tech 1999), because both estuaries have geologic nickel sources. Furthermore, within the South Bay, sediment concentrations for copper in the surface are nearly twice that of a deep core sample while the nickel concentrations are similar. Despite nickel-removal procedures used at municipal waste treatment facilities, the occasional exceedances for nickel have occurred. The treated water (5.8 ppb total-Ni) is released into the lower portion of South Bay (8.3 ppb total-Ni) (Tetra Tech 1999). Considering this concentration relationship, and the much greater volume of the receiving waters relative to the municipal effluent, it appears unlikely that anthropogenic point-source inputs are imposing nickel exceedances in South Bay. These values are 4.1 ppb and 5.2 ppb for copper, respectively, indicating that non-point source inputs (likely brake pad dust) elevate the copper concentration.

Average nickel concentrations in the continental crust are in the range of 20 ppm (Taylor and McLennan 1985). Within serpentinite deposits, this value is consistently much higher, reaching up to 3000 ppm Ni (Rytuba and Kleinkopf 1995). Weathering of these deposits produces point and non-point effluent with elevated concentrations of nickel (Rytuba et al. 2000). After the weathered sediment settles in the Bay (Fig. 1), particle-associated contaminants can be remobilized by adsorbent dissolution or ligand-enhanced desorption. This remobilization into the solution phase results in a gradient between pore-water and bottom-water concentrations that facilitates a net flux of dissolved nickel from the sediment to the overlying water column. Since an internal source of nickel is considered to be a likely contributor to observed elevated concentrations (Flegal et al. 1991), benthic-flux calculations were made to determine its importance relative to other inputs.

While copper exhibited temporal variability in benthic-flux direction (both into and out of the sediment) (Topping et al. 2001, Kuwabara et al. 1996), nickel flux was nearly always positive: Measured benthic flux from 42 of 46 core incubations indicated a flux out of the sediment (Fig. 2). Furthermore, the largest positive flux estimates are nearly an order of magnitude greater than the uncommonly observed negative flux estimates.

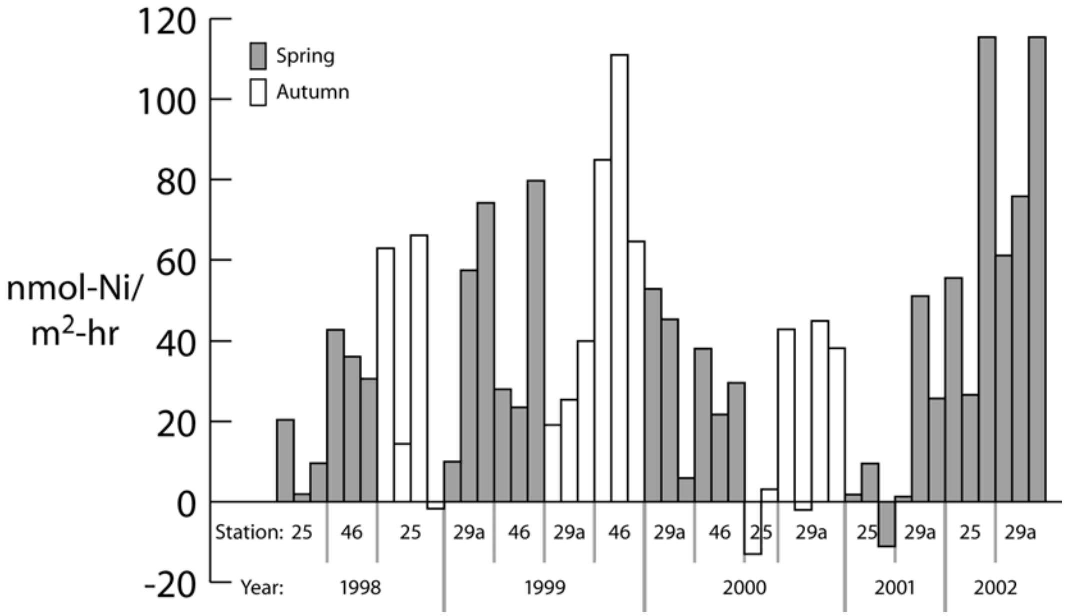

Figure 2. Consistently Positive Nickel Flux: Positive values (in nanomoles of nickel per square meter of sediment surface per hour) indicate flux from the sediment into the water-column. USGS station numbers for the San Francisco Bay are listed on the abscissa. Station 29a is a deep main channel station, while 25 and 46 are shoal stations (Fig. 1).

Using the South Bay surface area (south of the San Francisco-Oakland Bay Bridge) estimate of 554 km^2 (Cheng and Gartner, 1985), benthic-flux estimates can be areally averaged to the same units used in loading estimates (kg/day). Using data from forty-six unique core incubations, spanning four years and three South Bay sites, the average benthic flux load was 29 kg-Ni/day, with a 95% confidence interval of ±7 kg-Ni/day. This estimate is much larger than the major municipal point-source input of ~3 kg-Ni/day by the San Jose/ Santa Clara Water Pollution Control Plant for 1999 (Topping et al. 2001). The benthic flux estimates are lower but of similar magnitude (Fig. 3) to non-point source storm water runoff estimates for the surrounding watersheds (~56 kg-Ni/day) (Davis et al. 2000). The runoff value was derived by combining seven different sub-watersheds, or "hydrologic units" as defined by the authors. These units include significant rivers such as the Guadalupe River, Coyote Creek, Alameda Creek and San Francisquito Creek (Fig. 1). Similar to benthic flux, the weathering of serpentinite is likely a major contributor to this surface runoff estimate.

In addition, this runoff estimate is seasonally variable because local annual rainfall totals are dominated by the wet months. Between November and April, approximately 90% of the annual rainfall occurs (Cayan et al. 1991). Simplifying the water year into two halves, it could be estimated that nickel loading from storm-water runoff averages only 11 kg-Ni/day from May through October, and 101 kg-Ni/day during the wet months. The benthic flux estimate proved to be seasonally consistent: 29.3 ± 14.4 kg-Ni/day for autumn cores; 29.5 ± 9.3 kg-Ni/day for spring cores. These results indicate that benthic flux is likely the dominant source of dissolved nickel to South Bay during the dry months.

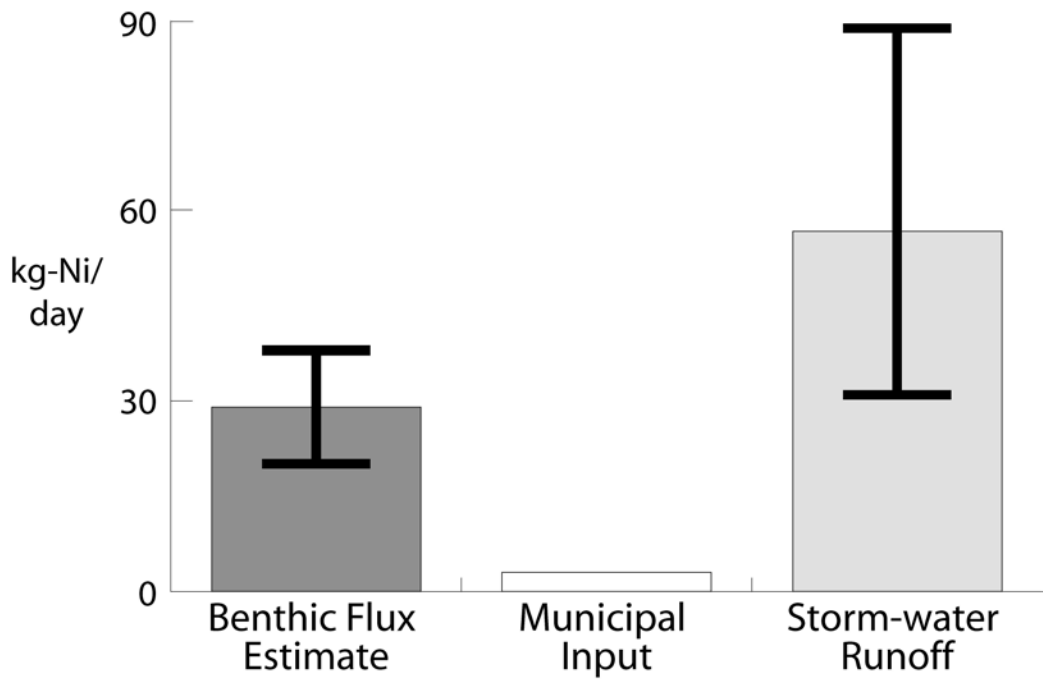

Figure 3. Comparison of dissolved nickel loading sources: Error bar for benthic-flux estimate represents 95% confidence interval; error bar for storm-water runoff estimate (Davis et al. 2000) represents the authors' estimate for the load variability, but does not include certain confounding factors (e.g. interannual variability).

The bioavailable portion of the dissolved nickel is paramount when considering potential toxicological ramifications. Studies have shown that dissolved nickel in South Bay is about 35-50% strongly organically-complexed and not bioavailable (Donat et al. 1994). By contrast, 75% of dissolved nickel in wastewater effluent is strongly complexed (Sedlak et al. 1997). This disparity between ambient and point-source nickel speciation, along with the fact that storm-water runoff is marginalized during the dry months, suggests the potential importance of benthic interactions in regulating nickel bioavailability in South Bay from May through October.

Since these results indicate that the magnitude of the measured benthic-flux of nickel is significant relative to major fresh-water inputs, metal remobilization from the sediment is an important consideration in determining realistic responses to future load-allocation strategies for nickel into the estuary. Our results suggest that benthic interaction with the overlying water column is one of the primary processes regulating dissolved-nickel concentrations in the South Bay.

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REFERENCES

Caffrey JM, Hammond DE, Kuwabara JS, Miller LG, Twilley RR (1996), Benthic processes in San Francisco Bay: the role of organic inputs and bioturbation. In: Hollibaugh JT (ed) San Francisco Bay – the Ecosystem, p 425-442

Cayan DR, McLain DR, Nichols WD, DiLeo-Stevens JS (1991) Monthly climatic time series data for the Pacific Ocean and western Americas. U.S. Geological Survey Open File Report 91-92

Cheng RT, Gartner JW (1985) Harmonic analysis of tides and tidal current in South San Francisco Bay, California. Est Coast and Shelf Sci 21:57-74

Davis JA, McKee LJ, Leatherbarrow JE, Daum TH (2000) Contaminant loads from stormwater to coastal waters in the San Francisco Bay region, San Francisco Estuary Institute, Richmond, CA

Donat JR, Lao KA, Bruland KW (1994) Speciation of dissolved copper and nickel in South San Francisco Bay: a multi-method approach. Anal Chim Acta 284: 547-571

Flegal AR, Smith GJ, Gill GA, Sanudo-Wilhelmy S, Anderson, LCD (1991) Dissolved trace element cycles in the San Francisco Bay estuary. Mar Chem 36:329-363

Kuwabara JS, Chang CCY, Khechfe AI, Hunter YR (1996) Importance of dissolved sulfides and organic substances in controlling the chemical speciation of heavy metals in San Francisco Bay. In: Hollibaugh JT (ed) San Francisco Bay – the Ecosystem, p 157-172

Rytuba JJ, Kleinkopf MD (1995) Silica-Carbonate Hg Deposits. In: duBray EA (ed) U.S. Geological Survey Open-File Report 95-831

Rytuba JJ, Enderlin D, Ashley R, Seal R, Hunerlach MP (2000) Evolution of the McLaughlin Gold Mine Pit Lakes, California. In: Proceeding from the Fifth International Conference on Acid Rock Drainage, Denver, CO, May 21-24, 2000, p 367-378

Sedlak DL, Phinney JT, Bedsworth WW (1997) Strongly complexed Cu and Ni in wastewater effluents and surface runoff. Environ Sci Technol 31:3010-3016

Taylor SR, McLennan SM (1985) The continental crust: Its composition and evolution. Blackwell Scientific Publications, Oxford

Tetra Tech (1999) Conceptual model report for copper and nickel in lower South San Francisco Bay. Tetra Tech, Inc., Lafayette, CA

Topping BR, Kuwabara JS (1999) Flow-injection-ICP-MS method applied to benthic-flux studies of San Francisco Bay. In: Buxton H (ed) U.S. Geological Survey Water Resources Investigation Report 99-4018B, p 131

Topping BR, Kuwabara JS, Parchaso F, Hager SH, Arnsberg AJ, Murphy F (2001) Benthic flux of dissolved nickel into the water column of South San Francisco Bay. U.S. Geological Survey Open-File Report 01-89

Willie S (2000) Interlaboratory study for trace elements in San Francisco Bay estuarine water, National Research Council, Ottawa, Canada, p 29